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Atmospheric Carbonic Acid, its Estimation and Variation.

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Lecture

DELIVERED BY

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Historical Remarks: Joseph Black. It is just 150 years since Professor Joseph Black first demonstrated the presence of Carbonic Acid in the air. Black was recognised as one of the most expert investigators of his day, and his discovery of carbonic acid or "fixed air" as he called it was one of his several most important achievements. His investigations on the Carbonic Acid in air and on the composition of carbonate of lime were done when he was a young man at Glasgow University. On his promotion to be Professor of Chemistry at Edinburgh University Black appears to have given up original research work, and to have devoted all his energies to teaching an art in which he became as accomplished and as successful as he was in investigation work.

Black and those who followed him appear to have enormously over-estimated the amount of Carbonic Acid in the air. From 50 to 1,000 volumes of Carbonic Acid per 10,000 volumes of air were supposed to be present by the various investigators who worked at the subject during the 18th century.

John Dalton. It was not till the inventive genius of John Dalton of Manchester was brought to bear on the subject that approximately accurate results as to the amount present were obtained. Dalton was engaged in investigating the subject in 1802, and he soon demonstrated that instead of the atmosphere containing one per cent. of Carbonic Acid it contained less than one-tenth of a per cent. by weight, *i.e.*, 6·8 volumes per 10,000 volumes.

Dalton collected the air in a bottle of a capacity of 471 cub. in.—far too small as we now know. Lime water or Baryta water was added in known amount and of known strength, and after absorption of CO_2 the solution was titrated against dilute sulphuric acid. He collected the air sample by first filling the bottle with water and then emptying out the water in the situation where he wanted to collect his air sample. This was a bad plan, and the error it gave rise to was demonstrated by Dalton's distinguished pupil, Hadfield, in 1828.

Hadfield. Hadfield improved the method of collection by using a dry bottle and filling it with air by means of a bellows.

Dalton's process with the modifications suggested by Hadfield is as good and even better than many of the processes described in our text-books to-day. I will ask you shortly to consider whether we in this country are not entitled to speak of Dalton's method rather than Pettenkofer's.

De Saussure. Between 1810 and 1830 De Saussure, of Geneva, published the results of his work with a gravimetric method. He precipitated the Carbonic Acid in about 34 litres of air and weighed the resulting barium carbonate. By this method he showed that the mean amount of CO_2 in air was about 4·03 volumes per 10,000 volumes of air.

Pettenkofer. The next important and far-reaching researches in atmospheric carbonic acid were made by Pettenkofer by a method almost identical with that of John Dalton and his pupils—a dry bottle, the air forced in by means of a bellows, Lime or Baryta water used as an absorbent and "any non-volatile dilute acid for titration." Angus Smith says that the use of the oxalic acid for titration is the essential of the Pettenkofer process, but obviously that is wrong for Pettenkofer himself says "any non-volatile acid" will do.

In view of all the circumstances I now ask you whether we, in this country, should not associate Dalton's name with the bottle method of determining CO_2?

Angus Smith. You have in Manchester another very interesting link in the investigation of Atmosphere Carbonic Acid, for it was here that Angus Smith did much of his work on the subject of the variation of Carbonic Acid in the air. Those who may not have read his "Air and Rain" will find that it contains much valuable information in regard to Carbonic Acid.

Having now indicated very briefly the scope of the older work on Atmospheric Carbonic Acid, I will next describe some of the more recent methods and afterwards the results.

Methods in Use at the Present Time. The methods may for the sake of convenience be divided into (*a*) those devised to secure the greatest possible accuracy irrespective of the amount of trouble involved, and (*b*) those designed for practicable purposes.

Those of us who are engaged in practical public health work, and who may be required to make Carbonic Acid determinations in examining as to the efficiency of methods of ventilation should have a knowledge of the degree of accuracy of the process we employ. Most of our text-books are vague and insufficient, and it will probably be found that the best results will be obtained by studying carefully, first, those methods which have the merit of scientific accuracy and then seeing how our available working methods differ in accuracy. In this way many errors will be avoided and confidence in our results obtained.

Haldane and Pembrey's Method. Of the accurate methods probably one of the best is that described by Dr. J. S. Haldane, F.R.S., and Dr. M. S. Pembrey in the "Philosophical Magazine," Vol. xxix., p. 306. In this method one or more absorption tubes are used filled with carefully prepared soda lime. In order to prevent the absorption of moisture from the air by the soda lime the air is passed through absorption tubes filled with pumice soaked in sulphuric acid. These observers aspirated 90 litres of air at the rate of one litre per minute. The soda lime tubes were weighed on a chemical balance before and after the absorption, and the difference taken as the weight of CO_2 in the air. As an additional precaution control absorption tubes should be submitted to the same temperature and other conditions without being used for CO_2 absorption.

In comparing the accuracy of this method with the bottle method Haldane and Pembrey show that for air which is pure or relatively pure, the excess of CO_2 as indicated by the latter varies from 7 to 18 per cent.

There are obvious disadvantages in the use of the method for practical purposes. The amount of air 30 to 90 litres is inconveniently large, and the time required for the absorption of the Carbonic Acid too long for every-day work.

I recommend the method as one eminently suitable for checking the accuracy of any of the ordinary working tests. Since it is possible that any of us may now be required to take action and possibly prosecute on our results of CO_2 estimation, it is most important to be able to check our work against a reliable method.

Demonstration of the method was here given.

Dalton's Method and Modifications of It. The Dalton (or Pettenkofer) method has now been so improved as to be a reliable and quite satisfactory means of estimating the amount of CO_2 in air if care and attention are paid to the numerous details. A good deal of experience is required in order to avoid serious error.

Collection of Samples. (*a*) The *bottle used for the collection* of the sample of air should be large—at least capable of holding five litres and have a wide mouth. Its capacity should be accurately measured by filling it with distilled water at 60°F. to the top. An indiarubber cap is more convenient than any form of cork or stopper. The bottle should be washed clean and dried inside thoroughly. It is advisable that acid be not used for washing these collecting bottles as it is difficult to get rid of traces of it.

(*b*) The air may be filled into the bottle by using a *bellows* as a force pump, or by using it as an *aspirator*. The most convenient and best form is that suggested by Angus Smith. Such a bellows folds into small space, and when used as an aspirator enables the operator to place the bottle where the sample has to be collected while he himself may stand seven or eight feet away. (It is most important at all times to bear in mind the danger of error arising from one's own expired air.) The above form of bellows aspirator is used extensively in obtaining samples of gases in chemical works. One stroke of the bellows aspirates 1 cubic-foot of air. If the bellows is filled 10 times when working with a 5-litre bottle the air in the bottle will have been changed at least 20 times—sufficient to obtain a reliable sample.

Reagents and Procedure. After filling with air the bottle is capped and taken to the laboratory where 100c.c. *Baryta water* is added by means of a pipette. The absorption of the CO_2 is allowed to go on for an hour, the Baryta solution being shaken up at intervals. The Baryta solution is removed from the absorption bottle with the same pipette and filled into a bottle of about 120c.c. capacity from which all CO_2 has been previously removed. This bottle has a well-vaselined stopper and the contained solution is allowed to deposit its carbonate by remaining quiescent for 24 hours.

Every precaution must be taken to prevent so sensitive a solution coming in contact with air containing CO_2 and specially with the expired air of the operator. When dealing with samples of pure air if the text-book descriptions of the process are followed the error will never be less than 25 per cent. and often will be as much as 50 per cent.

The solutions required as are follows:—

1. *Baryta solution* about 1 per cent. This should be stored in a large bottle having a soda lime inlet for air, and a special long outlet to admit of the pipettes being filled direct without suction being required.

2. The acid which I think is the best for all-round work is twice recrystalized

oxalic acid of the strength 1·41 grammes per litre.* This should be dissolved in boiled-out distilled water so as to free it as far as practicable from CO_2. Much of the commercial acid is impure. It is easier to obtain an approximately correct oxalic acid than a hydrochloric acid when working in a laboratory where correct solutions are not kept in stock. Weak solutions of oxalic acid have the great disadvantage of not keeping well. They should therefore always be used fresh. Each c.c. of this acid = 1 volume of CO_2 per 10,000 when using 25c.c. of Baryta.

The titration. 25c.c. of the Baryta solution should be placed in a flask from which all CO_2 has been washed out and titrated with the oxalic acid, phenolphthalein being used as an indicator. Having obtained the accurate titre of the Baryta exactly similar procedure should be adopted with 25c.c. of the supernatent solution used as an absorbent. The 100c.c. allows of at least three such determinations. Quickness and care in preventing expired air gaining access to the Baryta is all important.

At one time the error in my experiment with the Dalton method amounted to 0·9 volume of CO_2 per 10,000. With the precautions I have above described it is less than 0·25 volume of CO_2 per 10,000 volumes of air when dealing with pure air. I have not estimated what the error is when impure air is being dealt with but anticipate it will not be greater.

Demonstration of method was given here.

Method Adopted by the Author. Another very convenient method which I have used a good deal within recent years and found even less liable to error is as follows. The air is collected in an empty india-rubber balloon inside a wide-mouthed bottle by being pumped in by means of a hand-bellows. The india-rubber bag, filled with the air, is taken and attached to an absorption tube so arranged that the air is passed through the Baryta solution in small bubbles at a slow rate.

The *absorption tube* was first devised by Pettenkofer and recently greatly improved by Dr. Gibson.

This absorption tube is filled to a mark with the Baryta solution in the same way as one would fill a pipette from the Baryta stock-bottle. Five litres of the air are drawn from the india-rubber bag through the absorption tube and into a graduated aspirator bottle. The absorption is very complete. Its efficiency may be controlled by means of a second similar tube connected with the first. After the whole of the air was passed through the contained Baryta solution is treated in exactly the same manner as that from the bottle. The advantage of this method is the ease with which an accurate sample can be obtained. A more accurate sample is obtained than with the bottle method. Its chief disadvantage lies in the fact that the passage of the air through the absorption tube takes at least an hour.

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* The acid should be tested against a standard acid and proved to be $C_2H_2O_4 2H_2O$.

The above absorption tube is admirably adapted for the estimation of CO_2 in ground air. The absorption tube is directly attached to the air tube in the ground and the air is measured by means of a bottle aspirator.

Letts' and Blake's Method. Quite recently Letts and Blake have described an important modification of the Dalton process which will be found useful in ascertaining one's own working error by the ordinary process.

All bottles used to contain or receive Baryta solution were coated with paraffin wax to prevent the Baryta acting on the glass. The collecting bottles were filled by a method of exhaustion, 50c.c. of Baryta were run in from a special measuring pipette so that the Baryta did not come in contact with the air at all. After absorption is complete the whole of the Baryta is sucked into a special vacuous flask and then titrated. The whole process is carried out with the least possible chance of error. It is however tedious and the apparatus expensive. With known volumes of CO_2 added to air these observers found that the mean error per 10,000 volumes of air was only 0·04 volumes.

Haldane's Method. No account of modern methods for the estimation of CO_2 would be complete without a reference to the excellent work done by Dr. J. S. Haldane, F.R.S. in this connection.

The apparatus which he has devised is most ingenious and excellent in its arrangements. It enables an estimation of the amount of CO_2 in the air to be made in about five minutes, and in addition it has the advantage of enabling the examination to be made on the spot and without any calculation.

Dr. Haldane's description of the apparatus is so complete in the *Journal of Hygiene*, or in the report on the "Ventilation of Factories and Workshops," that it will be unnecessary to give here a detailed description of it.

Briefly it consists of an accurately graduated measuring pipette which allows of exactly 25c.c. of air to be admitted for examination. Having collected the amount of air the CO_2 is absorbed in a caustic potash solution. After complete abstraction of CO_2 the volume of the air is again read off at the same temperature and pressure. The difference between the first and second readings giving the volumes of CO_2 per 10,000 volumes of air.

This appears to be very simple and easy of application, but in practice great care is required to ensure that the air under examination is kept at exactly the same temperature and pressure and that the whole of the apparatus is in good working order.

My own personal experience with the apparatus has not been very great though I have used it at intervals during the past three years. I have had some obviously inaccurate results when I least expected them, and it is the fear of a repetition of these results which makes me stick to one of the older methods which, though much more tedious, is, I think, more under control.

Demonstration of Haldane's apparatus was given here.

There are on the market many *other varieties of apparatus* for estimating the amount of atmospheric CO_2. Most of these have some defect rendering them inaccurate or else they are mere modifications of the Dalton process.

Corrections for Temperature and Pressure. A point which will arise in these determinations is as to whether it is necessary to correct for temperature and pressure. For all work where scientific accuracy is required such corrections must be made. On the other hand in estimations made with a view to ascertaining the amount of CO_2 for the purpose of judging of the sufficiency or otherwise of the means of ventilation correction to normal temperature and pressure is unnecessary as the temperature and pressure at which the samples are analysed are relatively uniform and therefore the results are fairly comparable.

Personal Error. A much more important point is to know accurately the amount of one's own experimental error. This will vary for each observer. If a uniform amount of care is observed the amount of the error will be consistently uniform. My own error with the Dalton method is 0·24 volume of CO_2 per 10,000 volumes of air, *i.e.*, if I find 3·24 volumes of CO_2 in air I know I am dealing with air containing three volumes only; if 20·74 the corrected figure would be 20·5.

It is most important to test one's results against such a gravimetric method as that of Haldane and Pembrey or that of Professor Letts and Mr. Blake.

The effect of experimental error is indicated by the statements in most of our text-books that pure air contains about four volumes per 10,000, when, as a fact, such air contains rather less than three volumes—an error of about 33 per cent. when pure air is being dealt with, or of 7 per cent. when air containing 14 volumes of CO_2 per 10,000.

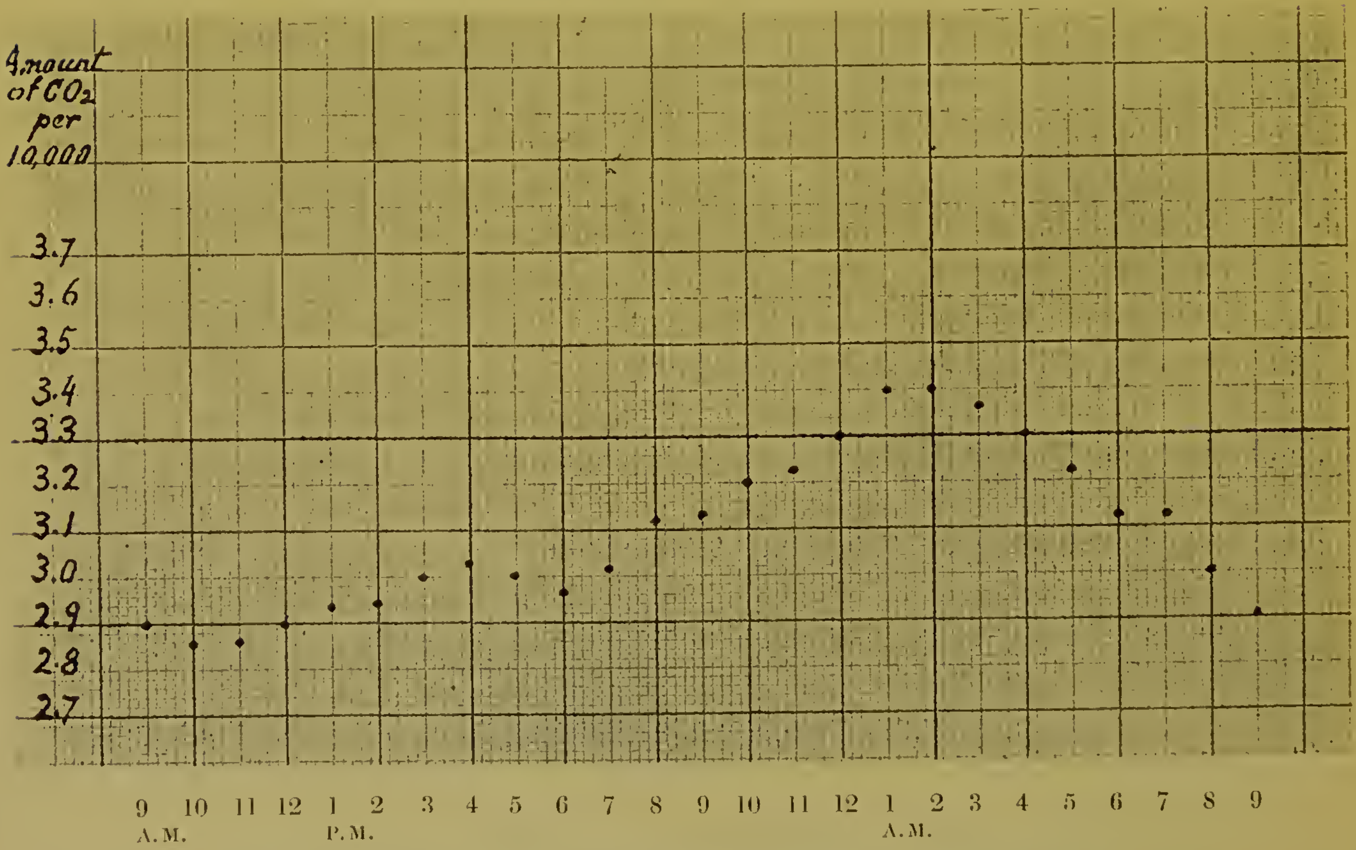
Amount of Carbonic Acid in Air. Pure air was shown by Thorpe in 1866 to contain 2·95 volumes of CO_2. Numerous other observers who have avoided the most obvious errors in the Dalton method have obtained similar results, the two most recent in this country being:—

1. Haldane, who gives the following results:—

		No. of Analyses.	Average CO_2 per 10,000 vols.	
April 1st to September 30th	day......	29	2·88	2·98
	night ...	22	3·08	
December to January	day......	6	2·99	3·00
	night . .	5	3·01	
2. Prof. Letts and Mr. Blake		46		2·91

Variations Due to Seasons and Weather. The variation in the amount of carbonic acid in the pure air of the country is extremely small from day to day. In the observations of Haldane noted above it varied from 2·58 to 3·55 volumes per 10,000 at different times of the year, and in different weather conditions. It is difficult to make use of the results of other workers for they are not strictly comparable owing to variations in methods.

My own observations are not sufficiently numerous but they indicate that during clear weather in summer-time the variation is slight if the observations be taken at the same time each day.



Hourly variation in amount of CO_2 in atmosphere in Summer time.

All observers are agreed that there is in summer-time more CO_2 in the air at night than during the day, due to the fact that plants only take up CO_2 during daylight and also to the escape of ground air from the warm soil into the cold atmosphere. There appears to be little doubt, however, that the amount of this variation is small and for practical purposes unimportant. My own figures show an absolute variation of 0·5 volume, *i.e.*, from 2·9 to 3·4.

But while the variations in atmospheric CO_2 in pure air are small and practically unimportant, there are many conditions in nature which produce departures from the normal.

Influence of Towns. All observers are agreed that the air of towns contains appreciably more CO_2 than does that of the country. The following are a few averages:—

Observer.	*District.*	*Town.*	*Country.*
Angus Smith	Manchester	4·3	3·69
Muntz	Paris	3·19	2·84
Spring and Roland ...	Liege	3·35	2·94
Williams	Sheffield	3·85	3·29

Influence of Large Water Surfaces. The amount of CO_2 is least over large water surfaces such as the ocean, and the diurnal variation is, as expected, absent.

Influence of Vegetation. The amount of CO_2 taken up by green leaves is very considerable. Under favourable conditions as much as $\frac{1}{2}$ litre of CO_2 can be decomposed by a square metre of leaf surface. This ought to play a very important part in influencing the amount of CO_2 in air, but air currents both upwards and lateral reduce the effect so that in practice the variation is unimportant.

Influence of Fog. Angus Smith was probably the first to demonstrate the importance of fog in increasing the amount of CO_2 in the atmosphere. His figures are for Manchester: During fogs, 6·79 vols. CO_2; ordinary weather, 4·03 vols. CO_2.

Dr. W. J. Russell, F.R.S., made observations at St. Bartholomew's Hospital in 1882—84, and found that as much as 14·1 vols. of CO_2 may be found in a London fog, and that the mean results of 29 examinations showed 7·2 vols. of CO_2 per 10,000 vols.

The importance of recognising this fact will be obvious when estimations of the amount of CO_2 in the air are made for ventilation purposes.

The excess of CO_2 during fogs has been shown to be due to the accumulation of the products of combustion and decomposition due to the absence of air currents.

Influence of Rain. Rain appears to diminish the amount of CO_2 in the air by washing out a small proportion.

Von Fodor, at Buda Pest, gives the following results:—

	Before rain.	*During rain.*
1877	4·6	4·15
1878	3·86	3·53
1879	3·68	3·60

Influence of Season. There is a slight increase in CO_2 in winter. Peterman, working at Gembloux, in Belgium, gives the following:—

Spring	2·95
Summer	2·91
Autumn	2·92
Winter	2·95

Storage of CO_2 in the Soil. The great carbonic acid storehouse is the soil. Here bacterial life is constantly producing enormous quantities of the gas which concentrates in the lower layers, and in the upper layers is diluted by transfusion. From this storehouse CO_2 is given off during the night and during windy weather. Von Fodor, who has done so much in regard to the CO_2 in the soil has published a diagram of the season changes in the amount of CO_2 in the soil at varying depths.

My own observations indicate that the amount yielded by the soil varies very much in different soils and even in any particular soil the amount varies enormously from year to year with temperature, rainfall, and wind.

Influence of Respiration and Combustion. The question of vitiation of air by CO_2 derived from combustion and respiration is from the practical point of view the most important source of CO_2. Here again some most excellent work has been done in Manchester by Mr. Francis Jones, who has published in his "Airs of rooms" a most important contribution to our knowledge of the influence of combustion and respiration on the air in rooms.

Any consideration of the effects produced by combustion in the air of rooms would lead us too far away from the subject proper of our lecture. The amount of CO_2 in air from combustion and respiration is indicated by the difference actually found between the air in the centre and that in the suburbs of a large City. Specially is this noticeable when the movement of the air is a slow one and when convection currents are reduced to a minimum by the presence of fog.

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